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LITHIUM-ION BATTERY PULSE/HIGH RATE DEMONSTRATION

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THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

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Performance of lithium-ion batteries at low temperatures and/or high rates is relatively poor due to high cell internal impedance. The ac impedance spectroscopy was utilized to determine the impedance characteristics of lithium-ion cells as a function of state-of-charge, temperature, and cycle number. From this impedance characterization, optimal pulse current discharge times and discharge battery temperatures were selected to enhance the lithium-ion battery discharge performance.

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1. SUMMARY

Performance of lithium-ion batteries at low temperatures and/or high rates is relatively poor due to high cell internal impedance. The ac impedance spectroscopy was utilized to determine the impedance characteristics of lithium-ion cells as a function of state-of-charge, temperature, and cycle number. From this impedance characterization, optimal pulse current discharge times and discharge cell temperatures were selected to enhance the lithium-ion cell discharge performance.

2. INTRODUCTION

Use of lithium-ion batteries in various applications is dependent on battery performance as a function of temperature, cycle life, and charge/discharge rate. Performance of lithium-ion batteries at low temperatures and/or high rates is, however, relatively poor due to high cell internal impedance[1-2]. One proposed method of enhancing the rate capability of lithium-ion batteries is by the use of pulsed currents. The length of the individual pulse is set short enough to minimize the effects of interfacial resistance. Furthermore, at very small time intervals (10s to 100s of μseconds), the charging/discharging of the battery electrochemical double layer further enhances the rate capability of the battery. Another method to enhance the rate capability would be to utilize the self-heating of lithium-ion batteries to reduce the battery's internal impedance to allow more efficient charging/discharging. Knowledge of the battery's impedance as a function of temperature, state-of-charge, cycle number, and the thermal properties of the battery are required to a priori predict the battery temperature history on charge/discharge.

This report focuses on the enhancement of the rate capability of a 5 Ahr lithium-ion cell at low temperatures by the use of pulse discharging.

3. METHODS, ASSUMPTIONS, AND PROCEDURES

Prismatic 5 Ahr lithium-ion cells were procured for testing. The cell composition of the cathode active materials consisted of $LiNi_xCo_{1-x}O_2$, as the main active material, the electrolytes were $LiPF_6$ organic solutions of suitable composition for low temperature operation, and the anode active materials were a synthetic graphite.

Electrochemical ac impedance measurements using an EG&G PAR Model 273A potentiostat/galvanostat with a Model 5210 lock-in amplifier were performed on the cells as received and during various states of charge, temperature, and cycle number.

Electrochemical cycling was performed at temperatures from –30 to +30 °C with a constant external cell environment temperature maintained by the use of a Tenney Jr. Environmental temperature chamber. Cell external temperatures were monitored by use of thermocouples. Cell charging was performed using a constant current to a given voltage and then constant voltage for a total charge time limit or taper current limit. Cell discharging was performed at a constant or pulsed current to an averaged cell cutoff voltage of 3.0 volts.

4. RESULTS AND DISCUSSIONS

4.1 Impedance Results

The main contribution to lithium-ion cell polarization at low temperatures is the interfacial resistance. Figure 1 clearly illustrates that for a given state-of-charge, the logarithm of the interfacial resistance is linear with inverse absolute temperature. This is indicative of an activated process with the activation energy determined from the slopes in Figure 1. For this type of cell, the interfacial resistance is highest at the end and beginning of the discharge cycle with the interfacial resistance remaining relatively constant during the rest of the discharge. While other types of lithium-ion cells have a shown a dependency of interfacial resistance with cycle number, this cell has shown little if any change in interfacial impedance with cycle number.

Figure 2 illustrates select Nyquist diagrams for the frequency ranges of 10-0.01 Hz (five points per decade), for temperatures of –10 and –30 °C, and 0 and 25 percent depth-of-discharge (DOD). The interfacial resistance numbers gathered for Figure 1 were determined from a commercial equivalent circuit fitting program utilizing a simple Zarc equivalent circuit[3-4]. From these Nyquist diagrams, the majority of the interfacial resistance is developed below ~10 Hz. Thus, it is hypothesized, that if one can cycle at a frequency higher than 10 Hz, much higher cell utilization may be obtained by the minimization of the interfacial resistances (neglecting developing concentration gradients).

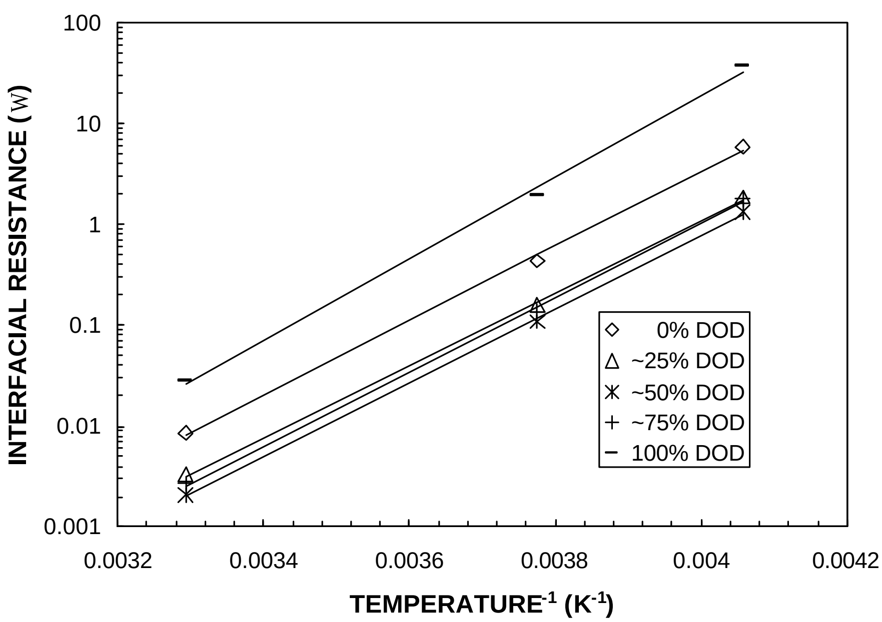

Figure 1. Interfacial Resistance for a 5 Ahr Lithium-Ion Cell as a Function of Temperature and State-of-Charge

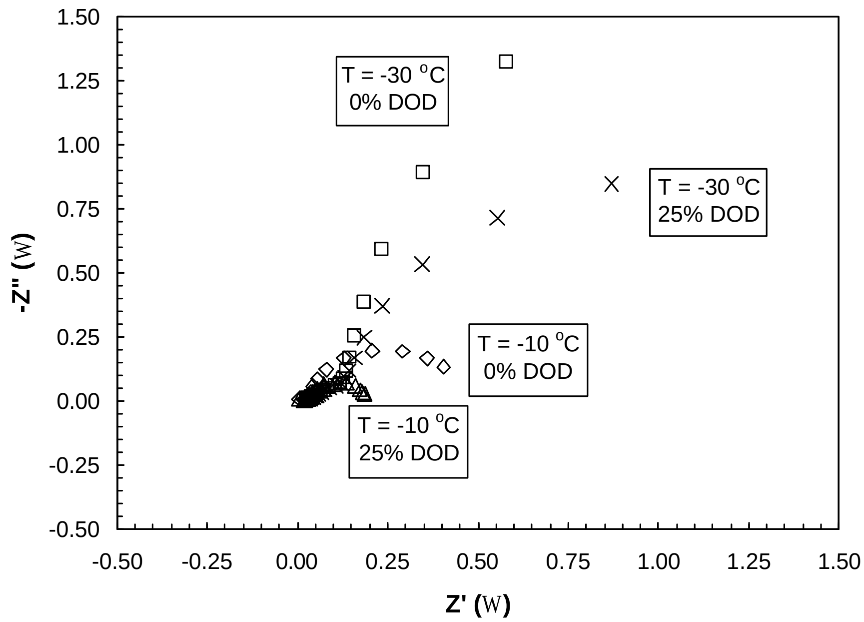

Figure 2. Select Nyquist Plots for a 5 Ahr Lithium-Ion Cell

4.2 Discharge Capacity Test Results

Figure 3 shows the capacity of the 5 Ahr lithium-ion cell under constant current discharges as a function of discharge rate and discharge temperature. Note that the cell was always charged at 30 °C. The cell performed rather well at the C rates except for at T = -30 °C where it took less than 30 seconds to reach the 3.0-volt discharge cutoff voltage. Figure 4 was an attempt to determine the maximum cell performance in the microsecond region for a given current. Due to the slow response of the solid-state load and the line inductance (~450 microseconds), the constant current cell performance in the 10s to 100s of microseconds was not determined. However, Figure 5 shows that by using the equivalent circuit parameters of a Zarc as determined from impedance spectroscopy, using a variable load resistance, and assuming constant cell open-circuit voltage, one can adequately simulate the cell discharge voltage for the 5-second discharge even at this high 10C discharge current. Similar curves have been generated for up to a 20C discharge rate for this cell. At lower temperatures, such as T = -10 °C shown in Figure 6, the interfacial resistance is not constant with discharge due to I^2R heating at the cathode particles/electrolyte interface. Detailed modeling of the transient heat/mass transfer occurring at cathode particles/electrolyte interface occurring for the 5-second discharge needs to be performed to determine the predicted interfacial temperatures and interfacial resistances.

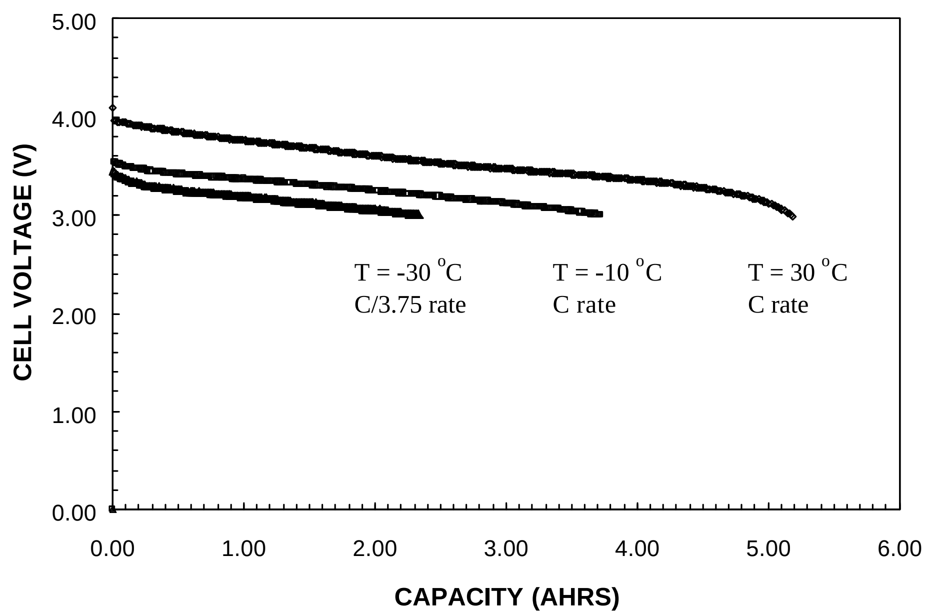

Figure 3. 5 Ahr Lithium-Ion Cell Discharge Capacity at Selected Temperatures and Continuous Discharge Rates

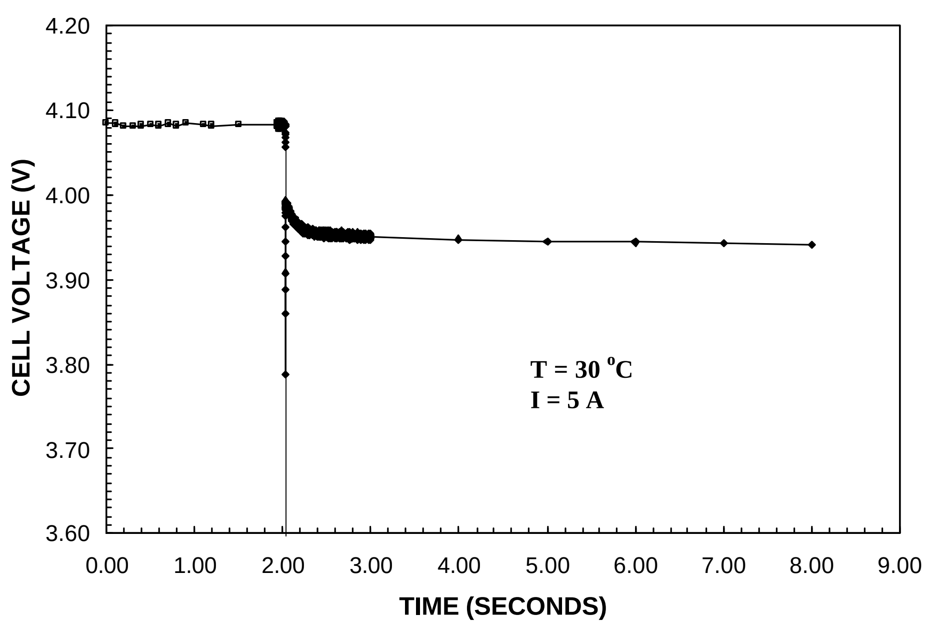

Figure 4. Discharge Voltage Response from a 5 Ahr Fully Charged Lithium-Ion Cell

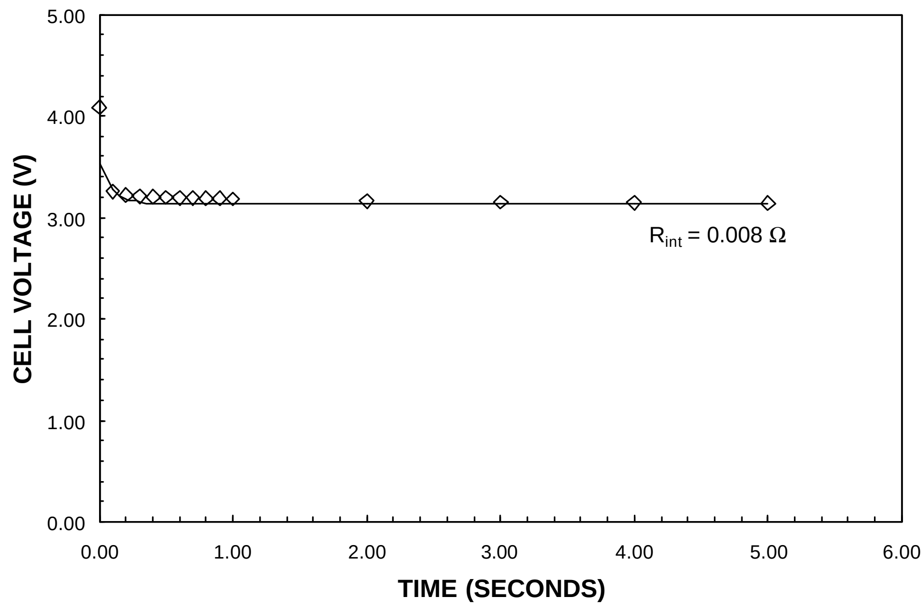

Figure 5. 5 Ahr Lithium-Ion Cell Discharge at T=30 °C, Full-Charge, and I = 50 A

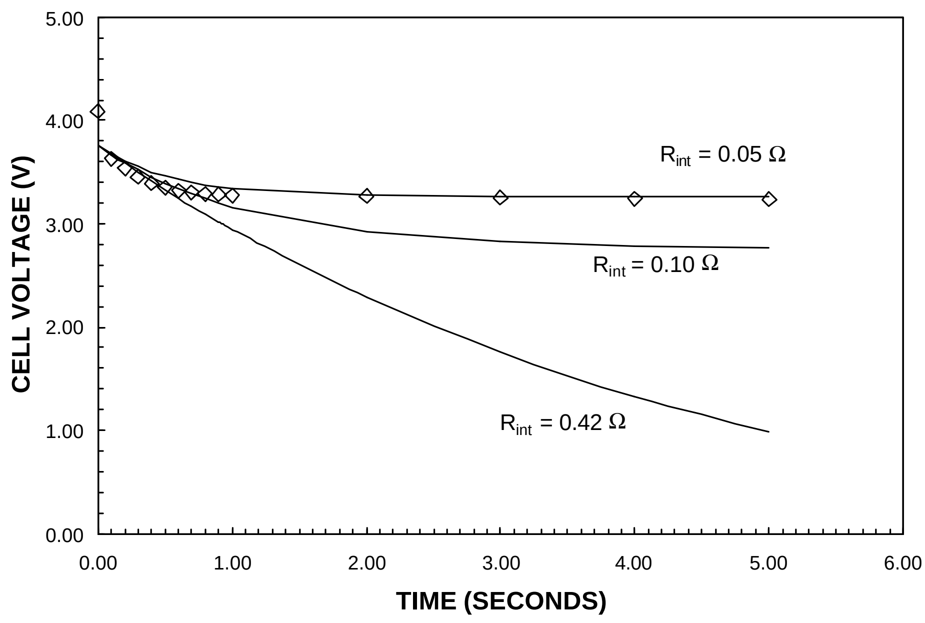

Figure 6. 5 Ahr Lithium-Ion Cell Discharge at T=-10 °C, Full Charge, and I = 10 A

Since the majority of interfacial resistance, as determined by ac impedance spectroscopy, occurs at frequencies below 10 Hz, pulse discharging was performed on a 5 Ahr lithium-ion cell at a frequency of 100 Hz with a duty cycle of 22 percent. The duty cycle was intended to be 50 percent, however, due to the slow response of the electronic load and line inductance, the resultant waveform was a duty cycle of ~22 percent. Figures 7 and 8 show the voltage waveforms as a result of pulse discharging. The cell capacities for this type of discharging are given in Table 1. Note that approximately half of the cell capacity can be delivered at –30 °C when pulsed at the 1.36 C rate but has zero capacity at the constant C current rate. From Figures 8 and 9, a maximum of 270 mV and 160 mV peak-to-peak of polarization is observed, respectively, for the 6.8-amp current pulse, which translates to about 40 and 24 milliohms of resistance, respectively. At this frequency, this resistance is due to mainly the electrolyte and contact resistance. Note that the cell in Figure 8 is more polarized than Figure 7 even though Figure 7 had been on discharge for a longer period of time. This is likely due to higher concentration gradients in the electrolyte and active material at the lower cell temperature in Figure 8 versus Figure 7. The interfacial impedance results determined using ac impedance spectroscopy are performed under minimal cell perturbation conditions (~1 mV rms) and doesn't account for nonlinear voltage losses occurring at high cell polarizations.

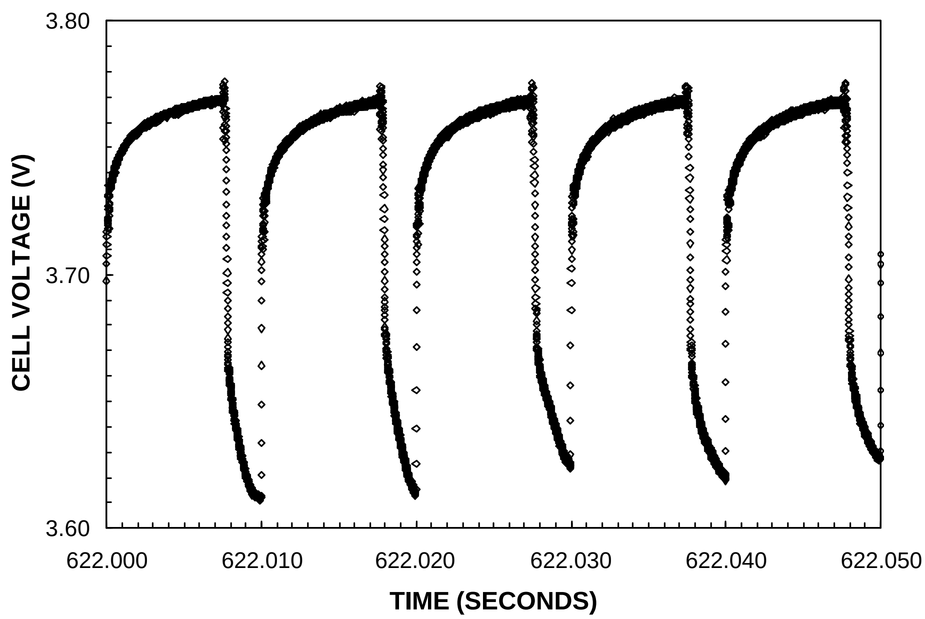

Figure 7. 5 Ahr Lithium-Ion Cell Voltage versus Time at T = -10 °C, I_{peak} = 6.8 A, Duty Cycle = 22 Percent, Period = 10 ms

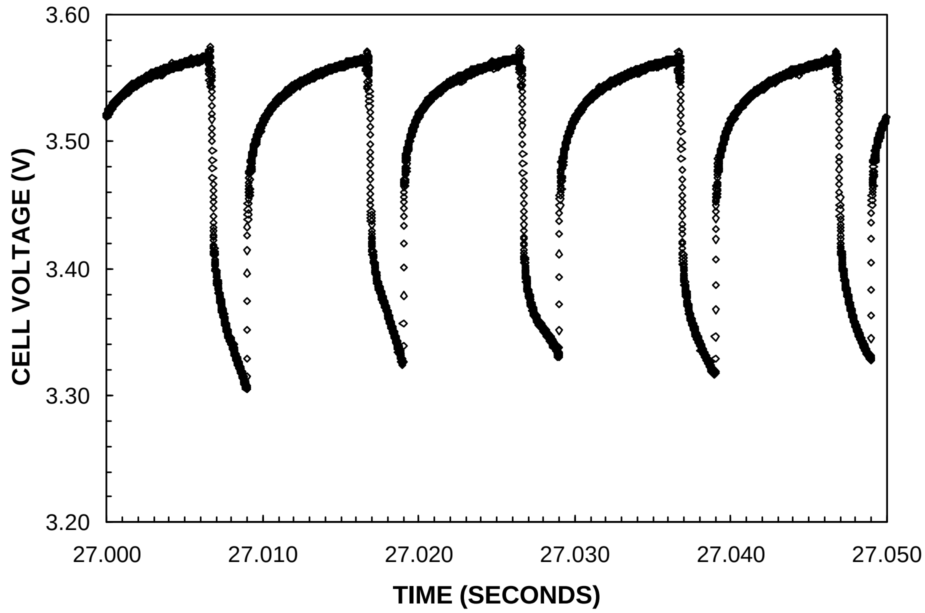

Figure 8. 5 Ahr Lithium-Ion Cell Voltage versus Time at T = -30 °C, I_{peak} = 6.8 A, Duty Cycle = 22 Percent, Period = 10 ms

Table 1. 5 Ahr Lithium-Ion Cell Capacity as a Function of Discharge Temperature and Rate

	CELL CAPACITY		
DISCHARGE RATE	T=30 °C	T=-10 °C	T=-30 °C
C rate discharge	5.19 Ahr	3.72 Ahr	~0 Ahr
1.36 C rate pulsed discharge	N/A	4.57 Ahr	2.25 Ahr

(note: all charging was performed at T = 30 °C)

5. CONCLUSIONS

Using ac impedance spectroscopy, the interfacial resistance of a prismatic 5 Ahr lithium-ion cell was determined as a function of temperature and state-of-charge. The interfacial resistance is highest at the end of discharge and at low temperatures. For a given state-of-charge, the interfacial resistance grows exponentially with decreasing temperature. The interfacial resistance, for this type of cell, did not visibly change with cycle number.

Pulse discharging of the 5 Ahr cell enhanced the rate capability of the cell. No cell capacity was observed under a constant current discharge at the C rate and a temperature of –30 °C while the pulsed current discharge at the same temperature and slightly higher current yielded almost half of the cell nominal capacity.

From the pulsed discharged voltage waveforms, the peak-to-peak voltage was highly dependent on cell temperature, indicating that at the current, frequency, and duty cycle utilized, liquid and solid state concentration gradients played a significant role in determining the cell polarization.

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